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THEORY OF SCALE PROCESSES ON ALLOYS

[Comment: The following report is a full translation of a lecture delivered by Prof Dr Karl Hauffe, director of the Institute for Physical Chemistry, before the Verein Deutscher Eisenhuettenleute in Duesseldorf on 1 October 1951. The lecture was published in Wissenschaftliche Zeitschrift der Universitaet Greifswald (Mathematics-Natural Sciences Series No 1), Volume I, Greifswald, 1951/1952.

Numbers in parentheses refer to items in author's bibliography.]

Introduction and Statement of the Problem

According to the equation of the chemical reaction, the formation of a metal oxide, sulfide, or halide by reaction of oxygen, sulfur vapor, or halogen gas with a metal at elevated temperature appears to be one of the simplest reactions. However, as oxidation research has shown, this is by no means true. In fact, there are considerable complications, since the reaction product often appears as a solid phase between the starting materials, and thus the reaction is often no longer controlled by phase boundary reactions but rather by diffusion phenomena in the oxide layer. For this reason, the center of research interest concerning the reaction mechanism has been an inquiry into the holes in these oxide, sulfide, and halide surface layers and the processes of diffusion through them.

These oxidation, sulfurization, and halogenation reactions at elevated temperatures will be designated as scale and tarnish phenomena. In the following discussion, we shall always speak of scale phenomena and scale strata when we are dealing with relatively thick and compact surface layers which are electrically neutral. The subject of this paper is restricted exclusively to scale phenomena. In contrast to these phenomena, the tarnish phenomena are characterized by surface layers ranging from thin to very thin designated as tarnish layers, in which diffusion phenomena have been produced using high electrical fields, as Mott and Cabrera (1) were able to show. While the last-named authors can easily explain both the logarithmic and the cubic tarnish law, in the case of the appearance of the scale layer, the parabolic scale law prevails. This first established in 1920 by Tammann (2) and then independently by Pilling and Bedworth (3) in 1923. If the concentrations or activities of the reactants at the phase boundaries of the scale layer are independent of time and are defined by a thermodynamic equilibrium, we have for the reaction rate, expressed as the increment of scale layer thickness $\Delta \xi$ per unit time, from the Frick diffusion law the following

$$\frac{d}{dt} (\Delta \xi) = \frac{k'}{\Delta \xi} \tag{I}$$

where k' is the scale constant. Integration gives

$$(\Delta \xi)^2 = 2k't. \tag{II}$$

In lieu of the determination of the layer thickness, the mass increment per sq cm, $\Delta m/q$, is often easier to determine. Equation II converts to

$$(\frac{\Delta m}{q})^2 = 2k't. \tag{III}$$

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The phenomena of diffusion through the crystallite of the scale layers are possible only if, extending an energy hypothesis of Frenkel, (4) one assumes that not all ions or atoms in a lattice are in their regular lattice places. According to Frenkel, for example, in a stoichiometrically compounded AgBr crystal, one finds a number of Ag ions in interstitial places with the formation of an equal number of unoccupied lattice points, so-called lattice vacancies. Figure 1 shows the well-known Frenkel lattice vacancy model, which can be considered valid for the silver halides.(5) Accordingly, an ion mobility through the vacancies without difficulty is understandable, since Ag ions can migrate either through the interstices (Figure 1, upper left) or through the lattice vacancies (Figure 1, upper right and lower left).

$$
\begin{array}{llllllll}
Ag^+ & Br^- & Ag^+ & Br^- & Ag^+ & Br^- & Ag^+ & Br^- \\
& Ag^+ \rightarrow & & & & & & \\
Br^- & Ag^+ & Br^- & Ag^+ & Br^- & \square & Br^- & Ag^+ \\
Ag^+ & Br^- & Ag^+ & Br^- & Ag^+ & Br^- & Ag^+ & Br^- \\
Br^- & Ag^+ & Br^- & Ag^+ & Br^- & Ag^+ & Br^- & Ag^+ \\
Ag^+ & Br^- & \square & Br^- & Ag^+ & Br^- & Ag^+ & Br^- \\
& & & & & Ag^+ & & \\
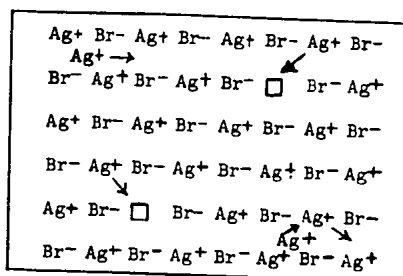Br^- & Ag^+ & Br^- & Ag^+ & Br^- & Ag^+ & Br^- & Ag^+
\end{array}
$$

Figure 1. The lattice vacancy model for AgBr according to Frenkel

The quantitative interrelationships were first adduced in the presentation of the general Wagner-Schottky lattice vacancy theory (6) by Wagner and his collaborators. On the basis of the halogenation of silver (7) as well as the sulfuration of silver (8) and iron (9) and the oxidation of copper, nickel, zinc (10) and iron (11), it has been possible to show that the metal, in the form of metal ions and electrons, often migrates from the metal to the oxidizing atmosphere through the scale layer. However, the other possibility of the diffusion of oxygen ions through the Fe_2O_3 and Fe_3O_4 to the metal has been demonstrated recently (11) for the oxidation of iron. The essentially independent migration of ions and electrons, which is related only to the condition of electrical neutrality, i.e., to the presence of equivalent amounts of ion and electron lattice vacancies per unit volume of scale layer, is of essential importance for the following analysis and has been determined quantitatively through the Wagner scale theory.(7,12)

Before we proceed to the quantitative evaluation of the Wagner scale formula, we should premise several general considerations concerning the formation of solid surface layers, the presence of which is fundamental for the application of the Wagner theory. The continual affinity of the metal for the surrounding atmosphere and the continual building up of the scale layer, which is characterized by the crystal structure and especially by the extent of lattice vacancy, bring about scale formation on the metals and alloys at various rates. Thus, the formation of a solid surface layer is, in general, conditional on the molar volume of the scale layer being greater than the atomic volume of the metal or alloy, because, if the volumetric ratio is the reverse, a very porous, spongy scale layer results.

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This general rule is subject to a modification, however, which has been mentioned by Frank and van der Maerve.(13) While, by way of an example, oxidation of copper, nickel, zinc, and iron generates a continuous well-bonded oxide layer on the metal, Hauffe and Rahmel (9) have not been able to observe a solid, sulfide surface layer upon sulfurization of nickel to NiS at 760° C. Because of the excessive difference in the volumes of the NiS and Ni and the resultant unfavorable conditions of formation of NiS energywise on the Ni lattice, the NiS layer appeared as a porous scale layer because of the constant "burstings." Furthermore, there are scale phenomena where the formation of a nonporous, solid scale layer has been ensured and where the parabolic time law has not been observed. For example, Hauffe and Pfeiffer (11) have been able to observe this phenomenon during the oxidation of iron in CO/CO_2 mixtures at $1,000^\circ$ C. Here the diffusion phenomena function

$$Me \rightarrow Me^{2+} + 2e^-$$
$$Me + O^{2-} \rightarrow MeO + 2e^-$$

$$\tfrac{1}{2}O_2^{(g)} \rightleftharpoons MeO + MeO'' + 2\ominus \quad (A)$$
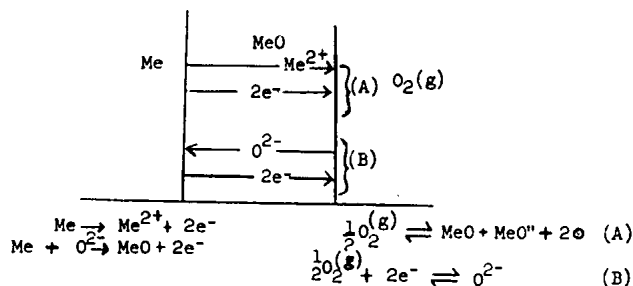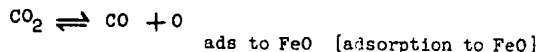$$\tfrac{1}{2}O_2^{(g)} + 2e^- \rightleftharpoons O^{2-} \quad (B)$$

Figure 2. The general oxidation scheme with possible diffusion and phase boundary phenomena.

more rapidly than the phase boundary reaction, i.e., the supply of oxygen according to the reaction

$$CO_2 \rightleftharpoons CO + O$$
ads to FeO   [adsorption to FeO]

In such cases, the application of the Wagner scale formula loses its validity.

By bypassing the derivative, which is necessary for the understanding of further considerations, we use the Wagner scale formula in its most general form

$$\frac{dn}{dt} = \left\{ \frac{300}{96500} \cdot \frac{1}{N\varepsilon} \int_{\mu_x^{(1)}}^{\mu_x^{(a)}} \frac{1}{(z_2)} (n_1 + n_2)n_3 \cdot \varkappa \cdot d\mu_x \right\} \frac{1}{\Delta\xi} \qquad (IVa)$$

$$= \frac{k''}{\Delta\xi} \cdot \qquad (IVb)$$

Here dn/dt signifies the amount of metal ions which migrated outward or the amount of metalloid ions which migrated inward toward the metal per sq cm and per second; $\Delta\xi$ designates the incremental increase in the thickness of the scale layer in cm; ε is the electron charge in absolute electrostatic units;

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and Z is the valence of the metalloid ions. Also, μ_x represents the chemical potential of the metalloid (e.g., oxygen); here the index (i) defines the phase boundary metal/oxide, and the index (a) defines the phase boundary oxide/oxygen (see Figure 2). κ is the electrical conductivity in ohm^{-1}· cm^{-1}; and n_1, n_2, and n_3 are the transfer numbers of the cations, anions, and electrons. The constant k", which is equal to the term in the braces in Equation IVa, is called the rational scale constant and states the reaction rate in equivalents per sq cm per second for a layer thickness of one cm.

As reported elsewhere (14), the chemical aspect based on the Wagner scale theory is to be considered, i.e., the breakdown of the scale phenomena into oxidatation, sulfuration, and halogenation reactions as well as those of secondary significance. We subdivide the scale phenomena in a more meaningful way into ion-conducting surface layers, where the capacity for partial electron conductivity is rate-determining, and into electron-conducting surface layers, where the ion conductivity determines the oxidation rate. As explained below in more detail, we distinguish between an electron defect conduction and an electron excess conduction in scale systems having electron-conducting surface layers, the knowledge of which leads to decisive predictions.

As is recognized from formula IVa, in the case of a scale system with an ion-conducting surface layer, perhaps AgBr $n_1 = 1$, a pure Ag ion conduction is shown, as has been indicated by the transfer measurements of Tubandt.(15) With $n_2 = 1$, one obtains from scale formula IVa the capacity for partial electron conductivity $n_3 \cdot \kappa = \kappa_3$ as the rate-determining factor of the entire bromination reaction. A reduction of the bromination rate can result only if the capacity for electron conductivity (equals concentration times mobility of the electron interference patterns) decreases. In another case, with a scale system with electron-conducting surface layer, e.g., in the oxidation of copper where Cu_2O is an electron defect conductor, $n_3 = 1$. This means that with $n_2 = 0$ and constant chemical potential or oxygen partial pressure, the oxidation rate is defined by the capacity for conducting Cu ions. According to these considerations, a control of the scale rate is possible simply by varying the rate determining partial conductivity for the diffusion in the scale layer.

Scale Phenomena on Alloys Having Ion-Conducting Surface Layers

On the basis of conductivity and transfer measurements on silver halides, it has been established that they are, as already mentioned above, typical ion conductors, wherein the Ag ions conduct the current through the lattice vacancies and interstices. According to the Frenkel lattice-vacancy concept, the following anomalous equilibrium can be assigned to silver bromide resulting from the bromination of silver as a result of its stoichiometric composition:
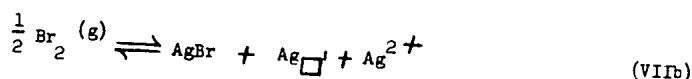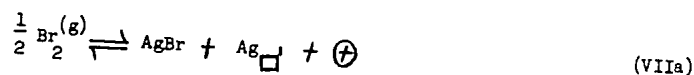
$$\text{Undisturbed AgBr crystal} \rightleftharpoons Ag_{\square}{}' + Ag_o \cdot \qquad (V)$$
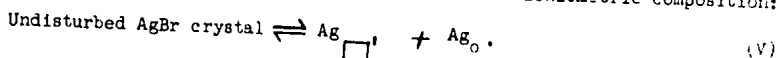
whereby a number of Ag ions, determined by the temperature, leave their lattice points and stand at the interstitial points. Interstitial ions, $Ag_o \cdot$, are formed with the production of an equal number of Ag ion lattice vacancies, $Ag_{\square}{}'$. Thus, the circle designates the occupation of an interstitial point, and the dot at the upper right designates the single positive charge on the entire lattice. Correspondingly, the box designates an unoccupied lattice point, and the line at the upper right indicates the single negative charge of the interference pattern. If x_{Ag_o}. means the concentration of the Ag ions on the interstitial points and $x_{Ag_{\square}'}$ the concentration of the ion lattice vacancies, then for the pure AgBr phase (index^o), it is true that

$$x^o{}_{Ag_o \cdot} = x^o{}_{Ag_{\square}'} \qquad (VI)$$

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If one now considers the change in the lattice-vacancy pattern of a AgBr crystal in a bromine atmosphere, one observes the appearance of an Ag deficiency. This deficiency is due to the fact that an equal number of Ag ions and electrons left their lattice points and, with the bromine atoms found on the surface, form an AgBr lattice extending outward, leaving behind an equivalent number of Ag ion lattice vacancies $Ag_{\square}'$ and electron defect places $\oplus$, which, according to a proposal by Wagner (16), have been represented by Ag^{2+} ions. The symbolic conversion equation for this is

$$\frac{1}{2} Br_2 (g) \rightleftharpoons AgBr \;+\; Ag_{\square}' \;+\; \oplus \qquad\qquad (VIIa)$$

$$\frac{1}{2} Br_2 (g) \rightleftharpoons AgBr \;+\; Ag_{\square}' + Ag^{2+} \qquad\qquad (VIIb)$$

Application of the law of mass action, with ideal ambient conditions assumed, leads from VIIa to

$$x_{Ag_{\square}'} \cdot x_{\oplus} \quad K \cdot p_{Br_2}^{\frac{1}{2}} \qquad\qquad (VIII)$$

From this it follows that for the capacity for partial electron conductivity $K_{\oplus}$,which is proportional to concentration of electron defect point $x_{\oplus}$, there is a proportionality with $p_{Br_2}^{\frac{1}{2}}$, while the Ag^+ (lattice vacancy concentration $x_{Ag_{\square}'}$) is practically independent of the bromine partial pressure, as a result of the high specific lattice-vacancy concentration of the AgBr lattice. Because, however, according to Equation IVa, the bromination rate of the silver is determined by the capacity for partial electron conductivity, the bromination rate of the silver must increase with the square root of the partial pressure of the bromine. According to Equation IVb, it follows that for the bromination rate constant k", as Wagner has been able to show experimentally,

$$k'' = \frac{300}{96500} \cdot K_{\oplus} \quad (p_{Br_2} = 1) \; \frac{RT}{N\epsilon} \cdot \sqrt{p_{Br_2}} \qquad\qquad (IX)$$

If the bromine partial pressure is kept constant, a decrease in the concentration of the electron defect points follows upon increase in the Ag $+$ lattice-vacancy concentration from VIII and, consequently, according to IX, there is a decrease in the bromination rate. Koch and Wagner (17) have shown by means of conductivity measurements that the Ag $+$ lattice-vacancy concentration is increased by the insertion of divalent Cd or Pb ions, since, on the basis of electrical neutrality (see Figure 3), an Ag lattice vacancy is produced for every foreign ion introduced into the AgBr lattice.
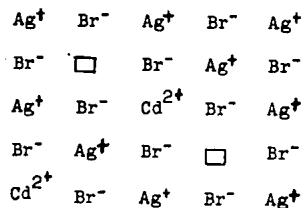
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$$
\begin{array}{ccccc}
Ag^+ & Br^- & Ag^+ & Br^- & Ag^+ \\
Br^- & \square & Br^- & Ag^+ & Br^- \\
Ag^+ & Br^- & Cd^{2+} & Br^- & Ag^+ \\
Br^- & Ag^+ & Br^- & \square & Br^- \\
Cd^{2+} & Br^- & Ag^+ & Br^- & Ag^+
\end{array}
$$

Figure 3. Lattice vacancy in a AgBr-CdBr$_2$ mixed crystal according to C. Wagner

As Teltow (18) showed, a maximum of about 25 mol % of CdBr$_2$ can be dissolved in AgBr at 330° C, whereupon a heterotypical mixed phase as indicated by Luves (19) is formed. The symbolic equation of the addition is

$$
CdBr_2 \rightleftharpoons Cd\bullet'(Ag) + Ag_\square' + 2AgBr \tag{X}
$$
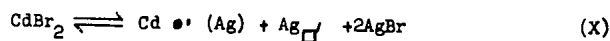
whereby, according to the Schotlky symbolsim, Cd $\bullet$' (Ag) means a Cd ion in a lattice position ordinarily occupied by Ag, which, as a result of the divalence of the cadmium ion, causes a positive charge on the entire interference pattern. On consideration of VIII and X, it follows that, for the ratio of the capacity of the partial electron conductivity of the pure AgBr phase $\varkappa_\oplus^0$ and the mixed phase $\varkappa_\oplus$,

$$
\frac{\varkappa_\oplus}{\varkappa_\oplus^0} = \frac{X^0 \, Ag_\square'}{X \, Ag_\square'} \tag{XI}
$$

From this equation, it follows that the ratio of the scale constants is

$$
\frac{k}{k^0} = \frac{X^\bullet \, Ag_\square'}{X \, Ag_\square'} \tag{XII}
$$

Here, the unknown concentration $X_{Ag_\square'}$ in the mixed crystal can be obtained from the law of mass action

$$
x_{Ag_\square'} \cdot x_{Ag_0'} = K \tag{XIII}
$$

as well as the condition of electrical neutrality

$$
x_{Ag_\square'} = x_{Ag_0'} + x_{Cd\bullet'(Ag)} \tag{XIV}
$$

to give:

$$
x_{Ag_\square'} = (1/2)x_{Cd\bullet'(Ag)} + \sqrt{\left[(1/2)x_{Cd\bullet'(Ag)}\right]^2 + K} \tag{XV}
$$

Considering the equality $x_{Cd\bullet'(Ag)} = x_{CdBr_2} = x_{Cd}$ (in the alloy), it follows from XII and XV that

$$
\frac{k}{k^0} = \frac{1}{\dfrac{x_{Cd}}{2x^0_{Ag_\square'}} + \left[\left(\dfrac{x_{Cd}}{2x^0_{Ag_\square'}}\right)^2 + 1\right]^{\frac{1}{2}}} \tag{XVI}
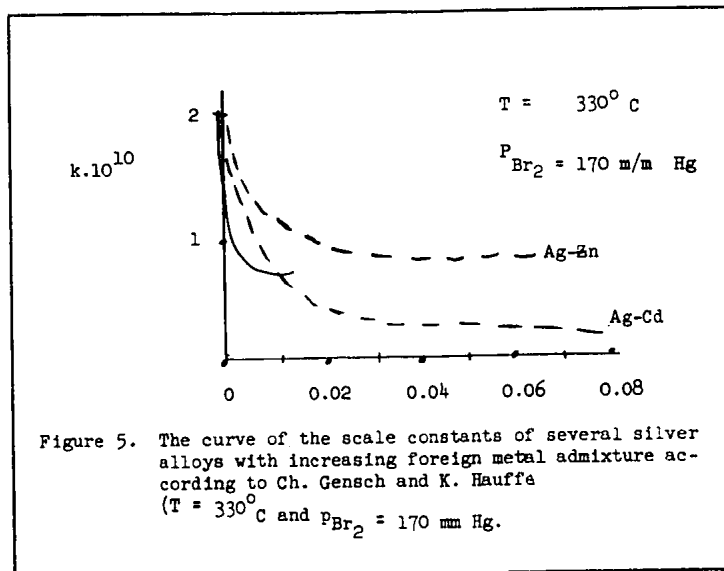$$

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As may be seen from Figure 4, the agreement between the measured k/k^o values and those calculated according to XVI is very satisfactory.(20)

Figure 4. The relationship of the ratio of scale constants k/k^o to the Cd content in the alloy according to K. Hauffe and Ch. Gensch (T - 330.° C. and $P_{Br_2} = 170$ mm Hg). Curve 1 represents experimental data. and curve 2 was calculated from equation XVI with the assumption of $x^o_{Ag_{\square'}} = 2.9.10^{-3}.$
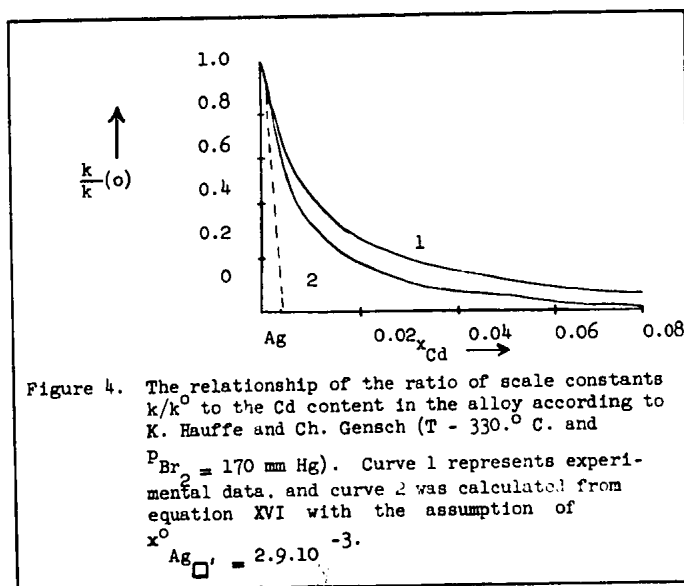
The same evaluations are valid for the bromination rate of Ag-Pb and Ag-Zn alloys.(21) However, as may be seen from Figure 5, the deviations in these cases are appreciable, especially with the Ag-Zn alloys. With the increasing solubility at 330° C in the series $ZnBr_2$ (about 1 mol%), $PbBr_2$ (about 8%), and $CdBr_2$ (about 25%), the scale constants decrease. A confirmation of the basic equations XII to XVI as adduced -- if only qualitatively -- by Himmler (22) in the controllability of the chlorination rate of silver in the presence of a $PbCl_2$ or $CdCl_2$ -- saturated chlorine atmosphere.

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Figure 5. The curve of the scale constants of several silver alloys with increasing foreign metal admixture according to Ch. Gensch and K. Hauffe ($T = 330^{\circ}$C and $p_{Br_2} = 170$ mm Hg.

The chances for the formation of more scale-stable Ag alloys than the Ag-Cd alloy with 5-8 atom % Cd are not great, if one considers that only those alloying additives come into question the valence of which is $z = 2$, and the ionic radius of which is $1.1 \pm 0.2^{\circ}$ A, so as to be able to guarantee a satisfactory solubility of the alloying metal bromide in AgBr and, thereby, a satisfactory increase in the concentration of Ag lattice vacancies in the scale layer. By use of the ionic radii of Goldschmidt, one can consider, from a practical view point, only the narrow choice of Cd (1.03), Pb (1.32), Cu (0.96), Tl (1.05), Sr (1.27), and perhaps La (1.22) and Ce (1.02). With these metals the possibilities for alloying are exhausted. The use of silver alloys with several alloying elements and the concomitant displacement of solubility of the less soluble metal ions by the more soluble metal ions in the Ag halide phase (23) result in a worsening rather than an improvement in the scale stability. To what extent foreign alloy surface layers in the form of thin Al_2O_3 and BeO layers on silver alloys inhibit scale formation (24) cannot be discussed within the framework of the present work.

## Scale Phenomena on Metal Alloys Having Electron Conducting Surfaces

According to the general scale formula IVa, the oxidation rate of this scale system with constant oxygen partial pressure and constant temperature is determined by the ion partial conductivity $\varkappa_{ion}$ and especially the cation partial conductivity $\varkappa_1 = \varkappa$ (metal ion), which is proportional to the mobility and the concentration of lattice vacancies of the metal ions. If one considers the mobility of the metal ions through the lattice vacancies in first approximation as constant and independent of the foreign ion content, then the oxidation rate is a direct function of the lattice-vacancy concentration of the metal ion; i.e., by increasing the metal ion lattice-vacancy concentration in the scale layer, the oxidation rate is increased, and on reducing the concentration, the rate is decreased.

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Since the oxidation phenomena in the scale system having solid surface layers are in most cases controlled only by diffusion of the ions through the ion lattice vacancies in the scale layer, we must first occupy ourselves with the lattice vacancy phenomena in oxides and oxide mixed phases from the standpoint of the lattice-vacancy theory. A large number of oxides, sulfides, and other compounds have the capacity to dissolve a more or less high percentage of one of the admixtures in excess. This fact has been considered by Wagner, and he has developed quantitative relationships concerning the degree of lattice vacancy of nonstoichiometric compounds. While numerous oxides, for example, Cu_2O, NiO, FeO, Bi_2O_3, etc., have a metal deficiency, other oxides, such as ZnO, CdO, TiO_2, etc. have a metal excess. Although the first group of oxides has an equivalent number of electron defect points, because of the formation of cation lattice vacancies due to electrical neutrality, and is therefore designated as electron defect conductors, the second group of oxides has an equivalent number of quasi-free electrons, because of the presence of metal ions in the interstices or oxygen ion lattice vacancies, and is therefore designated as electron excess conductors. A third group of oxides, called self-semiconductors, is not considered of importance to the following scale phenomena, since in this case the ion lattice-vacancy ratios have not been adequately clarified. In accordance with the classification principle of the semiconductor theory, we will consider bipartition later and will first discuss the principal aspects of a scale system having an electron-excess-conducting surface layer.

1. Scale Phenomena in Metal Alloys Having Electron-Excess-Conducting Surface Layers

According to the symbolic lattice-vacancy equation, on dissociation of the oxygen in zinc oxide, Zn ions form in the interstices $Zn_0 \cdot$, and quasi-free electrons $\ominus$ are formed.

$$ZnO \rightleftharpoons Zn_0 \cdot + \ominus + \frac{1}{2} O_2^{(g)} \tag{XVII}$$
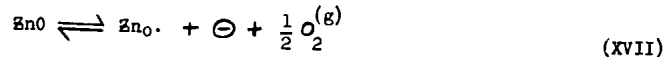
According to the law of mass action,

$$x_{Zn_0 \cdot} \cdot x_{\ominus} = K_{P_{O_2}}^{-\frac{1}{2}} \tag{XVIII}$$

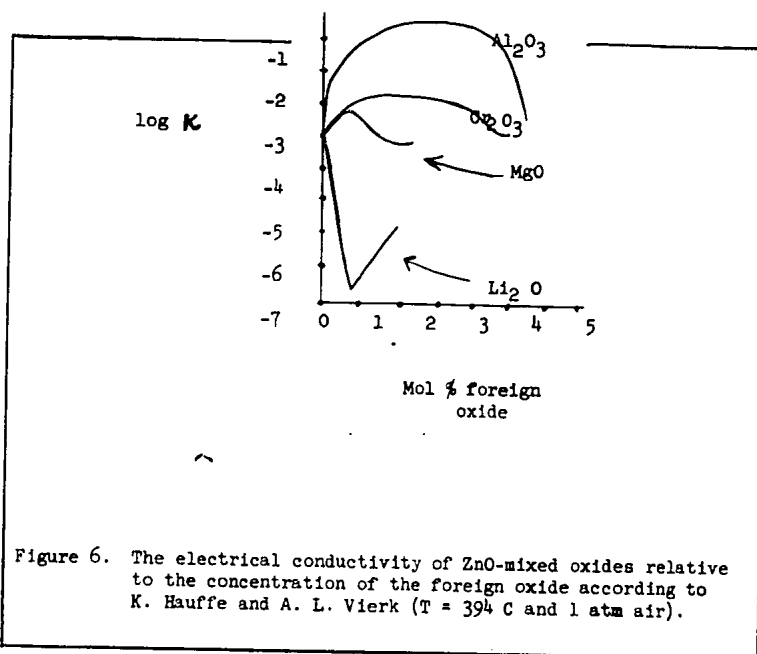and the equation $x_{Zn_0 \cdot} = x_{\ominus}$ gives for the electrical conductivity

$$k = \text{constant } P_{O_2}^{-\frac{1}{4}} \tag{XIX}$$

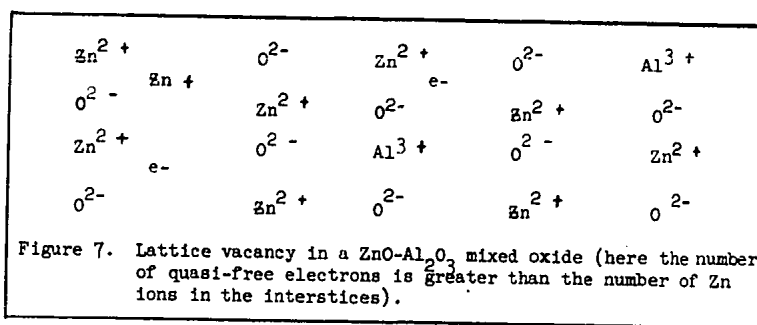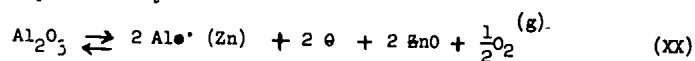i.e., the electrical conductivity must decrease with increasing oxygen partial pressure. It was found that k is

$$k \sim P_{O_2}^{-\frac{1}{4.5}} \quad \text{(See [25].)}$$

Wagner as well as Hauffe and Vierk (26) were able to show that, with small additions of Ga_2O_3, Al_2O_3, and Cr_2O_3, the electrical conductivity of ZnO increased with increasing foreign oxide content up to 10^3 (see Figure 6).

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Figure 6. The electrical conductivity of ZnO-mixed oxides relative to the concentration of the foreign oxide according to K. Hauffe and A. L. Vierk (T = 394 C and 1 atm air).

This finding may be understood on the basis of the condition of electrical neutrality and the law of mass action (XVIII). As is shown in Figure 7, on introduction of the trivalent Al ions, the Zn ions disappear into the interstices, and quasi-free electrons are formed. This may be represented by

$$Al_2O_3 \rightleftarrows 2\,Al\bullet\,(Zn) + 2\,\Theta + 2\,ZnO + \tfrac{1}{2}O_2^{(g)} \qquad (XX)$$

Figure 7. Lattice vacancy in a ZnO-Al$_2$O$_3$ mixed oxide (here the number of quasi-free electrons is greater than the number of Zn ions in the interstices).

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where Al •' (Zn) designates an Al ion in a Zn lattice place, and by combination of the equation of electrical neutrality,

$$x_{\ominus} = x_{Zno\cdot} + x_{Al\bullet\bullet(Zn)} \tag{XXI}$$

with the mass action equation (XVIII) at constant oxygen pressure; from which one obtains, as with the AgBr-CdBr$_2$ system, the ratio of the electrical conductivity of the ZnO mixed phase κ to the pure phase κ^o

$$\frac{\kappa}{\kappa^o} = \frac{x_{Al\bullet\bullet(Zn)}}{2\,x^o_\ominus} + \sqrt{\left(\frac{x_{Al\bullet\bullet(Zn)}}{2\,x^o_\ominus}\right)^2 + 1} \tag{XXII}$$

In accordance with the fact that the scale constants are inversely related to the conductivity values,

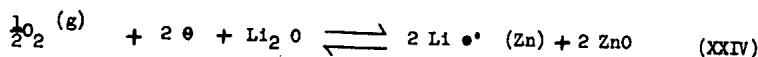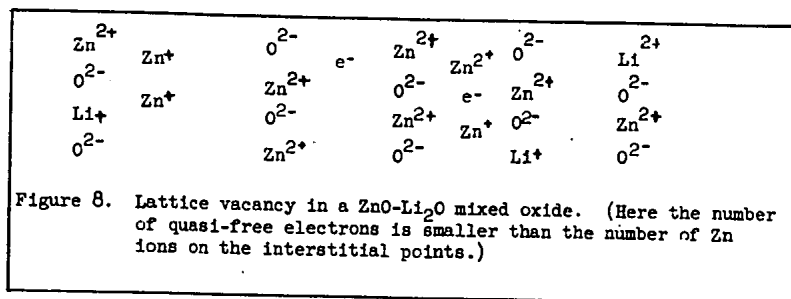$$\frac{k}{k^o} = \frac{\kappa^o}{\kappa}$$

and by assumption that

$$x_{Al\bullet\cdot(Zn)} = x_{Al} \gg x^o_\ominus = x^o_{Zn_{o\bullet}}$$

$$\frac{k}{k^o} \approx \frac{x^o_{Zno\cdot}}{x_{Al}} \tag{XXIII}$$

On introduction of Li$_2$O into the ZnO lattice, quasi-free electrons are nullified in accord with the equation

$$\tfrac{1}{2}O_2^{(g)} + 2\,\ominus + Li_2O \rightleftharpoons 2\,Li\bullet\cdot(Zn) + 2\,ZnO \tag{XXIV}$$

and the number of Zn ions in the interstitial points is increased (Figure 8).

Figure 8. Lattice vacancy in a ZnO-Li$_2$O mixed oxide. (Here the number of quasi-free electrons is smaller than the number of Zn ions on the interstitial points.)

This results in a decrease in the electrical conductivity (Figure 6) and an increase in the oxidation rate.

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$$\frac{k}{k^o} \approx \frac{X_{Li}}{X^o_{Zno}}$$

(XXV)

The validity of these expressions stems from the experimental data of Gensch and Hauffe (27) in Figure 9. Although the scale constant of spectroscopically pure zinc at 390°C in air and oxygen amounted to

$k^o = 9.10^{-10}$ ($g^2 . cm^{-4} .h^{-1}$), the scale constants of two Zn-Al alloys with 0.1 and 1.0 atom % Al were found to be less than 10^{-11}. Correspondingly, calculations using equation XXIII gave values of 4.10^{-11} and 4.10^{-12}. The scale constant of a Zn-Li alloy with 0.4 atom % Li under the same conditions was calculated to be of the order of $k = 10^{-7}$. It was found to be $k = 2.10^{-7}$. Also, this value agreed satisfactorily with the theory. The apparently remarkable behavior of the oxidation rate of zinc thallium alloys may mean that both Tl_2O and Tl_2O_3 are formed during the oxidation. As is seen from the oxidation curves, with small amounts of Tl in the alloy, the Tl_2O formation predominates; therefore there is an increase in the oxidation rate. With higher Tl contents, the Tl_2O_3 formation predominates; therefore there is a decrease in the oxidation rate compared with pure zinc (see figure 9).
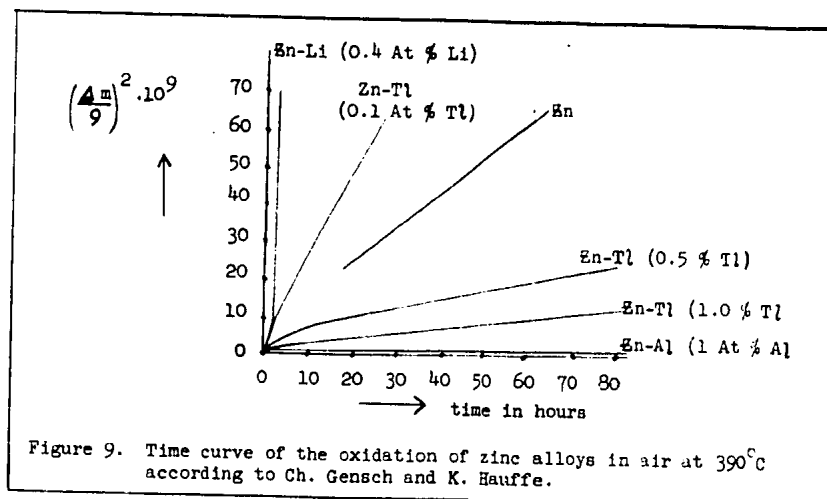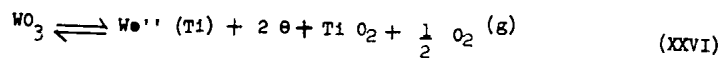

Figure 9. Time curve of the oxidation of zinc alloys in air at 390°C according to Ch. Gensch and K. Hauffe.
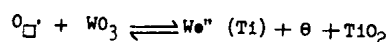
The usual metallic impurities in zinc, such as Ga, Al, Fe, etc., furnish cations of high valence upon oxidation, which, according to our theory, cause a decrease in the oxidation rate. On the basis of this fact, the high value communicated by us of $k^o = 9.10^{-10}$ in $g^2 . cm^{-4} . h-1$ or $f.10^{-15} cm^2 . sec^{-1}$ may be compared with values found with especially pure zinc by Wagner and Grünewald (28) of $6.7.10^{-16} cm^2 . sec^{-1}$.

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On the basis of these general theoretical considerations and the most recent conductivity measurements on TiO_2 - WO_3 mixed oxides by Hauffe and Grunewald (30), where the smallest addition of WO_3 induces a conductivity increase corresponding to electron-excess-conducting by the TiO_2, one can already predict with safety that with minimal addition of tungsten -- up to about 1 atom % -- the scale stability of titanium would be significantly increased. Research in this direction would be desirable. One can represent the introduction of WO_3 into TiO_2 in the following way:

$$WO_3 \rightleftharpoons W\bullet'' \ (Ti) + 2\ \theta + Ti\ O_2 + \frac{1}{2}\ O_2\ (g) \tag{XXVI}$$

or

$$O_{\square}\bullet + WO_3 \rightleftharpoons W\bullet'' \ (Ti) + \theta + TiO_2$$

$O_{\square}\bullet$ means an oxygen ion lattice vacancy with a trapped electron $(O_{\square}\bullet + \theta \rightleftharpoons O_{\square}\bullet)$

as a quasi-Farnsworth center. In accordance with the lattice-vacancy equilibrium proposed here,

$$TiO_2 \rightleftharpoons O_{\square}\bullet + \theta + \frac{1}{2}\ O_2\ (g) \tag{XXVII}$$

in contrast to the oxidation of zinc and zinc alloys, during the oxidation of titanium and titanium alloys oxygen ions and electrons migrate through the scale layer to the metal, and the diffusion of the oxygen ions determines the rate of growth of the scale.

2. Scale Phenomena on Metal Alloys Having Electron-Defect-Conducting Surface Layers

Electron-defect-conducting oxides or oxide mixed phases must result from the oxidation of, e.g., copper, nickel and their alloys. In contrast with the electron-excess-conducting oxides, there was found from conductivity measurements on NiO-mixed oxides that, on the addition of low valence cations, e.g., Li_2O (31), there was a logarithmic increase in electrical conductivity, while the introduction of high valence cations, e.g. Cr_2O_3, decreased the conductivity logarithmically. (32) (See Figures 10 and 11.)
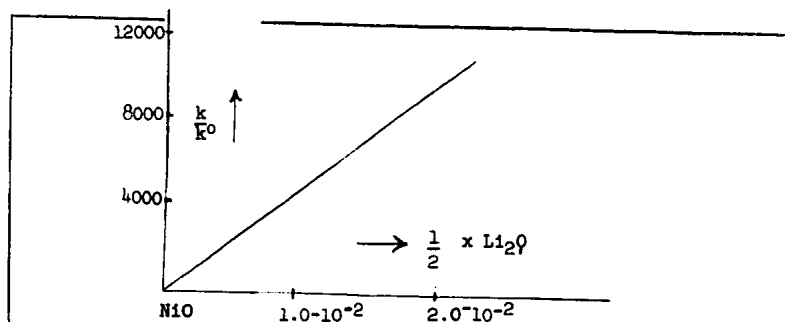

Figure 10. Increase in conductivity of NiO-Li_2O mixed oxides with increasing Li_2O content according to Vervey, Haayam and Romeyn, analyzed by K. Hauffe and A. L. Vierk. (After tempering at $1,200^{\circ}$C in 1 atm. O_2, measurements were made at 25° C.)
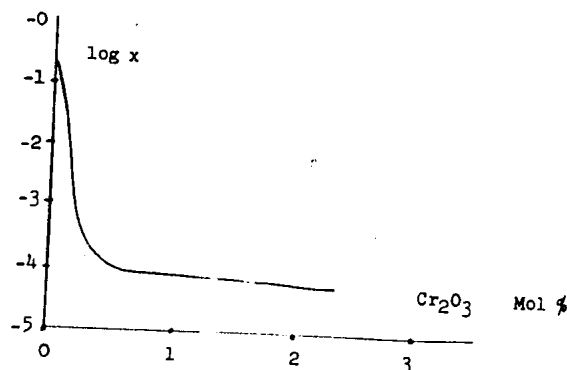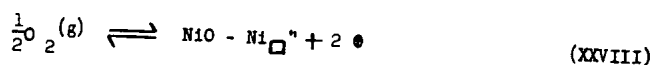
Figure 11. Decrease in conductivity of NiO-Cr_2O_3 mixed oxides with increasing Cr_2O_3 content according to K. Hauffe and J. Block (T = 400° C and 1 atm. air).

In accordance with the lattice-vacancy equilibrium for NiO

$$\tfrac{1}{2}O_2 \text{(g)} \rightleftharpoons NiO - Ni_{\square}'' + 2\bullet \qquad \text{(XXVIII)}$$
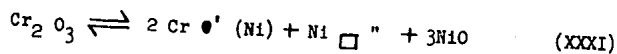
having the mass action relationship

$$X_{Ni_{\square}''} \cdot X_{\bullet}^2 = K \cdot P_{O_2}^{\tfrac{1}{2}} \qquad \text{(XXIX)}$$

and the condition $X_{Ni_{\square}''} = \tfrac{1}{2}X_{\bullet}$, the electrical conductivity must increase with the sixth root of the oxygen pressure.

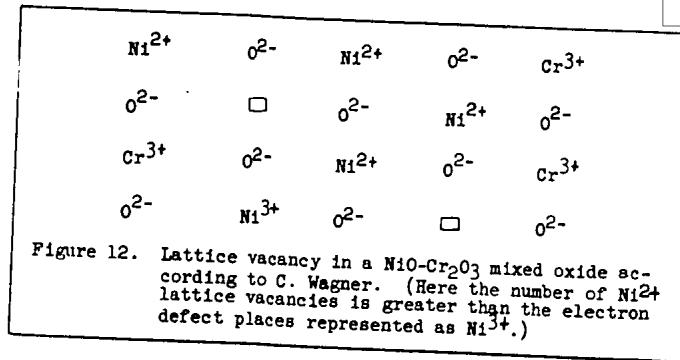$$K = \text{constant} \cdot P_{O_2}^{1/6} \qquad \text{(XXX)}$$

The data indicated $K \sim P_{O_2}^{\tfrac{1}{4}.5}$ (See [33].)

As the symbolic equation for the example of the addition of Cr_2O_3 to NiO shows

$$Cr_2O_3 \rightleftharpoons 2 Cr\bullet' (Ni) + Ni_{\square}'' + 3NiO \qquad \text{(XXXI)}$$

in the mixed oxide phase there must be an increase in Ni ion lattice vacancies $Ni_{\square}''$ and, according to the mass action relationship (XXIX), a decrease in the concentration of the electron defect places $X_{\bullet}$ (see Figure 12). If one considers the condition of electrical neutrality in the NiO-Cr_2O_3 scale layer of a nickel-chromium alloy

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Ni^{2+}	O^{2-}	Ni^{2+}	O^{2-}	Cr^{3+}
O^{2-}	□	O^{2-}	Ni^{2+}	O^{2-}
Cr^{3+}	O^{2-}	Ni^{2+}	O^{2-}	Cr^{3+}
O^{2-}	Ni^{3+}	O^{2-}	□	O^{2-}

Figure 12. Lattice vacancy in a $NiO-Cr_2O_3$ mixed oxide according to C. Wagner. (Here the number of Ni^{2+} lattice vacancies is greater than the electron defect places represented as Ni^{3+}.)

$$X_{Ni_\square"} = \frac{1}{2}x_\oplus + \frac{1}{2}x_{Cr\bullet'}(Ni) \qquad (XXXII)$$

with the approximation

$$X_{Ni_\square"} \approx \frac{1}{2}X_{Cr} \text{ (for } X_{Cr\bullet'}(Ni) = X_{Cr} \gg X^\circ_{Ni_\square"}), \qquad (XXXIII)$$

then it follows that the ratio of scale constants of a Ni-Cr alloy k to that for pure nickel k° is

$$\frac{k}{k^\circ} \approx \frac{X_{Cr}}{2X^\circ_{Ni_\square"}} \text{ (for } X_{Cr} \gg X^\circ_{Ni_\square"}) \qquad (XXXIV)$$

With disregard for a number of other empirical fundamentals of oxidation research on nickel alloys (34), the first oxidation researches were carried out with regard to the special working hypothesis of the lattice-vacancy phenomenon of Wagner and Zimens.(35) As is seen in Figure 13, the oxidation rate of nickel increases in accordance with equation XXXIV, then decreases rapidly with higher Cr contents (> 6 atom % Cr). This decrease evidently depends (36) on the spinel phase $NiCr_2O_4$, which increases with increasing Cr_2O_3 content in the scale layer where ion transposition phenomena occur only extremely slowly.

On the basis of minimal foreign metal admixtures, a reduction in the oxidation rate of nickel would be possible only by adding a monovalent metal such as Ag or Li. Oxidation research concerning Ni-Ag alloys, in contrast to the scale theory, has shown only slight reductions in the oxidation rate.(37)
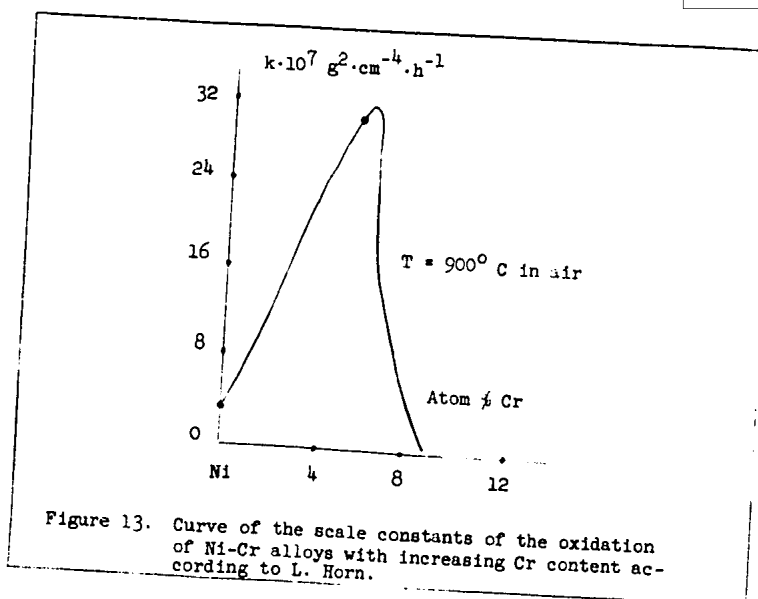
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Figure 13. Curve of the scale constants of the oxidation of Ni-Cr alloys with increasing Cr content according to L. Horn.

The reason may clearly lie in the excessively low solubility of Ag_2O in NiO, since the ionic radii of Ni with 0.78 and Ag with 1.1Å differ too greatly. On the other hand, the introduction of Li_2O may lead one to expect a significant decrease in the Ni^{2+} lattice-vacancy concentration $x_{Ni_{LT}}$ (Figure 14), and, thereby, a decrease in the oxidation rate as a result of the good solubility of Li_2O in NiO.

Figure 14. Lattice vacancy in a $NiO-Li_2O$ mixed oxide. (Here the number of Ni^{2+} lattice vacancies is smaller than the number of electron defect positions.)

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As in the addition of Cr_2O_3 to NiO, the addition of Li_2O together with the combination of the condition of electrical neutrality

$$X_{\oplus} = 2\, X_{Ni\,\square"} + X_{Li\bullet'\,(Ni)} \qquad\qquad \text{(XXXV)}$$

with the mass action equation (XXIX) for the case $X_{Li\bullet'\,(Ni)} = X_{Li} \gg X^o_{Ni\,\square"}$

The ratio of the scale constant k of the alloy to k^o of the pure nickel is as follows:

$$\frac{k}{k^o} \approx \left(\frac{X^o_{Ni\,\square"}}{X_{Li}}\right)^2 \qquad (\text{for } X_{Li\bullet'\,(Ni)} = X_{Li} \gg X^o_{Ni\,\square"})$$

$$\text{(XXXVI)}$$

Since the production of nickel-lithium alloys is not possible directly, one must choose another method for making NiO-Li_2O surface layers. Meijering and Rathenau (38) suggested a solution to this problem through their observation of an increase in the oxidation rate of metals and alloys in the presence of MoO_3 vapor. Similar observations had been reported by Leslie and Fontana.(39) Doubtless, the increase in the oxidation rate, especially that observed by the first pair of authors (38), could be traced to a decrease in melting point of the oxide layer caused by the introduction of the MoO_3. However, we see in these effects a further confirmation of our scale theory. According to the lattice-vacancy theory, the introduction of MoO_3 into an electron-defect-conducting oxide lattice must increase the number of cation lattice vacancies, which results in an increase in the oxidation rate. If our hypothesis is correct, then the oxidation rate is titanium, the oxide of which is an electron excess conductor, must decrease. Studies of this subject are in preparation. The Meijering and Rathenau process further has the possibility of effecting a reduction in the oxidation rate by use of another oxide, e.g., Li_2O. Preliminary studies of unoxidized pure nickel samples which were heated to 1,100° C in air containing Li_2O vapor showed a definite decrease in the oxidation rate (40) (Figure 15). By choice of suitable oxides, one is able to make stable scale layers on metals and alloys which ordinarily form scale of low stability without changing the composition of the alloy (patent). This point may be considered another example of the applicability of the Scale Theory of Alloys.
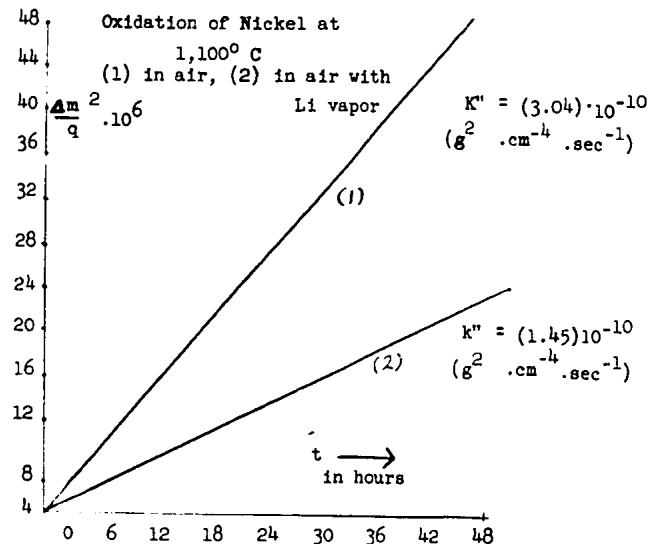
Figure 15. Decrease in the oxidation rate of nickel at $1,100^\circ$ C in air in the presence of Li_2O vapor according to K. Hauffe and H. Pfeiffer.

## Scale Phenomena With Rate-Determining Phase Boundary Reactions

Up to this point, only those scale phenomena have been considered in which the rate-determining component was the diffusion of ions through the scale layer. A larger number of scale systems, however, cannot be described by means of the lattice vacancy and scale theory. There are various reasons for this.

1. There are scale systems in which no solid surface layers develop upon oxidation, when the molar volume of the scale layer phase is less than the atomic volumes of the metal or alloy phase. The simplest examples are the oxidation phenomena on alkali and alkaline earth metals and their alloys.

2. There are scale systems in which the molar volume of the scale layer phase is greater than the atomic volume of the metal or alloy phase. The difference between the molar volume and atomic volume is so great that the possibililty of formation of a solid scale layer on the metal lattice is impossible from the standpoint of energy.(13) Here a porous surface layer forms because of continual "bursting," and, thus, through these pores the reacting gas can diffuse directly onto the metal subsurface. Such is the case with sulfuration of nickel and nickel alloys at 760°C. As the studies of Hauffe and Rahmel (41) have shown, in contrast to the sulfuration of iron, the parabolic law is not followed in this case but a linear time law of the form (see Figure 16)

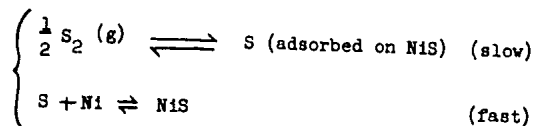$$\frac{\Delta m}{q} = k^* t$$

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As is also apparent from Figure 16, the sulfuration rate is extraordinarily high and increases in proportion to the square root of the pressure of the sulfur vapor. On the basis of microscopic investigations, the migration of the Ni ions and electrons can play only a secondary role.

Figure 16. The sulfuration-rate constant of nickel relative to the pressure of the sulfur vapor at 630° C according to K. Hauffe and A. Rahmel
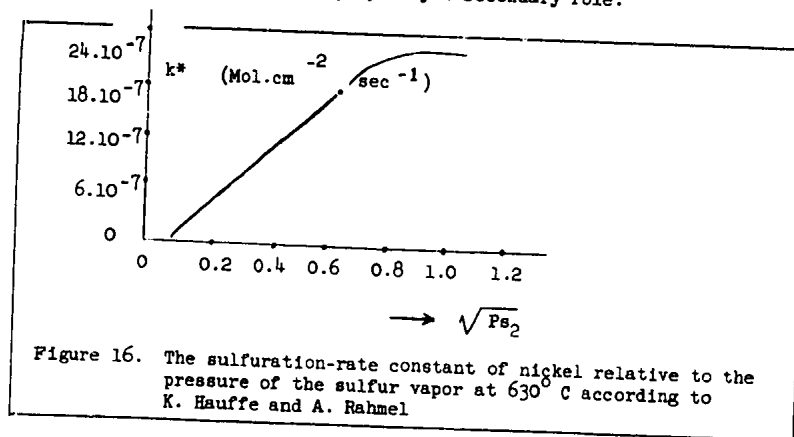
The diffusion of gaseous sulfur through the pores in the surface layer is the principal constituent of the reaction course. If one assumes the phase boundary reaction
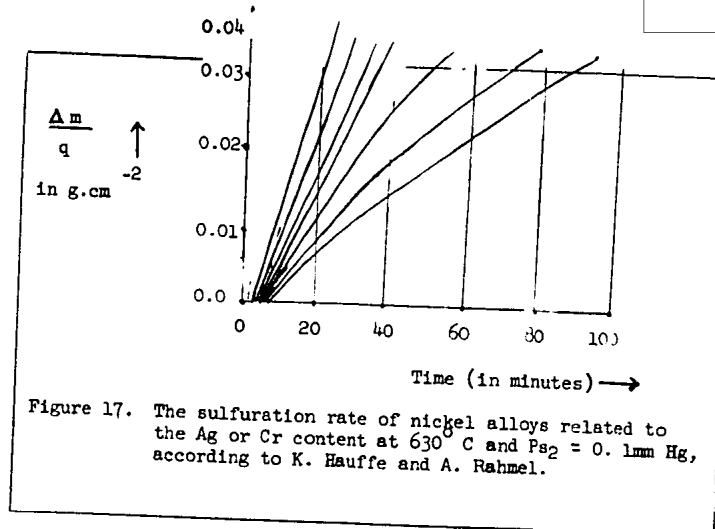
$$Ni + \frac{1}{2} S_2 \,^{(g)} \rightleftharpoons Ni\,S$$
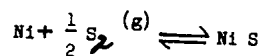
to be rate-determining, then a subdivision into the following partial reactions can be dealt with

$$\begin{cases} \frac{1}{2} S_2 \,(g) \rightleftharpoons S \text{ (adsorbed on NiS)} \quad \text{(slow)} \\ S + Ni \rightleftharpoons NiS \quad\quad\quad\quad\quad \text{(fast)} \end{cases}$$

of which the first is slower and is therefore rate-determining. The scale research on nickel alloys can be considered further support for the above hypothesis (Figure 17).

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Figure 17. The sulfuration rate of nickel alloys related to the Ag or Cr content at $630°$ C and Ps_2 = 0. 1mm Hg, according to K. Hauffe and A. Rahmel.

Here also the parabolic time law is not valid, but with most alloys the weight increase was proportional to the time. At constant sulfur pressure and constant temperature with nickel-silver alloys, the reaction increases per unit time with increasing silver content, while with nickel-chromium alloys a decrease in the sulfuration rate with increasing chromium content has been determined. The significance of pore formation in the surface layer has not yet been determined, since the lattice vacancy model of NiS is still being studied.

3. There are scale systems which form a solid surface layer where, however, above a certain temperature, a large number of overriding quasi-phase-boundary reactions are to be reckoned with. One such system is being studied at present by Hauffe and Pfeiffer (42) in which it has been found that, during the oxidation of Fe to FeO at $1,000°$ C, the slow reaction is the introduction of oxygen atoms, and the concomitant position shifts in the outer layer, according to Shottky (43), while at $900°$ C, the diffusion of Fe ions through the scale layer appears to be the rate-determining process.

The experimental data cited herein are taken from research work being financed by the State Planning Commission.

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